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(54) Polyglycerol Ester Synthesis

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ABSTRACT

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Polyols, in particular polyglycerol, are esterified using a fatty acid at atmospheric pressure or under slight vacuum. The reaction is carried out under an inert atmosphere at high temperatures (220°C-260°C) using an alkaline catalyst. When the free fatty acid level decreases to less than 1%, the reaction mixture is stripped of substantially all the water by reducing the pressure within the vessel. The alkaline mixture is then neutralized using a mild acid, e.g. phosphoric acid, while maintaining the high temperature and reduced pressure. The mixture is rapidly cooled to below 177°C after the neutralization step. The polyglycerol or polyol esters prepared via this process are of consistently high quality and are not subject to compositional changes during the process or on storage.

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POLYGLYCEROL ESTER SYNTHESIS

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Technical Field

5 This invention relates to the synthesis of polyol esters, in particular, polyglycerol fatty acid esters.

Background of the Invention

10 There are a number of processes available for synthesizing polyol esters. These include esterification with fatty acids with and without catalysis, as well as transesterification using triglycerides. Stenzel et al., Die Nahrung, 21, 429-441 (1977) reviews a number of literature references on the synthesis of polyglycerol fatty acid esters and their use. Phosphoric acid was found to be a favorable catalyst for esterification, as was
15 potassium or sodium hydroxide.

 One method for synthesizing polyol esters uses an ion exchange resin as a catalyst, see Canadian Patent 834,214, issued to Kuhrt et al. (1970). This process is said to yield pure monoesters of various polyglycerols. However, not all ion exchange resins are
20 approved for use in foods or for preparing food additives. Moreover, ion exchange resins are more expensive than alkaline catalysts.

 One of the problems with polyol esters, in particular polyglycerol esters, is the inconsistent quality of the product.
25 The polyol starting material is a mixture of dimers, trimers, tetramers, etc. of the starting alcohol. When this material is esterified with the fatty acid, the fatty acid will react with any of the free hydroxyl groups within the molecule. Thus, the esterified polyol is a mixture of monoesters, diesters, triesters, etc. Upon cooling in the presence of a catalyst or moisture,
30 these esters can rearrange not only by changing the position of

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the ester group within the molecule, but actual equilibration between diesters forming monoesters and triesters, etc. This equilibration changes the composition to a lower monoester content and increases the concentration of higher esters.

5 The degree of shift caused by interesterification is variable. The process herein eliminates the shift in composition and the batch-to-batch variations.

 In general, the more hydrophilic type of polyglycerol esters are more functional. These polyglycerol esters have a greater
10 number of free hydroxyl groups relative to the number of esterified hydroxyl groups.

 The esterification reaction is carried out under an inert atmosphere to obtain good color, flavor and odor characteristics. However, unless the mixture is properly neutralized to remove the
15 esterification catalyst, rearrangement will occur. That is, the polyglycerol ester will revert to polyol and higher esters (rearrangement).

 After the esterification is completed the catalyst is neutralized with a mild acid at $\sim 225^{\circ}\text{C}$. During the acid addition
20 or the cooling step which follows, rearrangement occurs. The composition shifts to a more lipophilic and therefore less functional product. The rearrangement releases free polyol which separates from the reaction mixture. The free polyol, if recycled into the product, contaminates the product and causes darkening of
25 the color. In particular, the recycle of polyglycerol results in additional undesirable polymerization of the glycerol. The polyol to fatty acid ratio also affects the ester composition but it is difficult to compensate for the shift caused by interesterification (i.e. rearrangement).

30 The process of this invention eliminates the uncontrolled interesterification and eliminates the need for polyol recycle. The process permits one to produce the most hydrophilic, most functional esters at the lowest polyol to fatty acid ratio. Since polyol is always more expensive than fatty acid, this process is
35 also more economical.

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Moreover, it has been found that the water from the reaction must be substantially removed before the neutralization of the catalyst to insure a product without reversion or random rearrangement.

5 Therefore, it is an object of the present invention to provide a process for producing polyol esters of consistently good color, flavor and odor characteristics. It is a further object of this invention to produce polyol esters which do not revert or rearrange upon standing.

10 It is an additional object of this invention to provide a process which utilizes inexpensive materials which are approved for preparation of food grade materials.

These and other objects will become apparent from reading the specification.

15 Unless specified herein, all percentages are by weight.

Brief Summary of the Invention

A process for esterifying a polyol comprising the steps of:

- 20 (1) reacting fatty acid and polyol under an inert atmosphere of temperatures from about 220°C to about 260°C and an absolute pressure of from about 500 mm to about 900 mm of mercury, in the presence of an alkaline catalyst;
- (2) reducing the pressure to less than 127 mm of mercury when the free fatty acid level is less than 1% to remove substantially all the water;
- 25 (3) neutralizing the alkaline catalyst with a weak acid under reduced pressure; and
- (4) rapidly cooling the reaction mixture to less than 177°C.

Detailed Description of Invention

The process herein is useful for the esterification of many
30 different polyols. Polyols are organic compounds containing more than one hydroxy group on the molecule. These include dihydroxyalkanes, glycerine, carbohydrates, sugar alcohols, polyglycerols, etc.

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The most preferred polyol is polyglycerol which is prepared by the polymerization of glycerine in the presence of either acid or base. The polyglycerols can contain from 2 to 20 glycerol moieties. Preferably, the polyglycerols will be those having from
5 2 to 15 glycerol moieties.

The polyglycerol compounds can be made by any synthetic method; the method of their preparation is not critical to the esterification process. See for example, U.S. 3,968,169 issued to Seiden and Martin (1976). However, the purer the starting
10 polyglycerol, the purer the polyglycerol ester will be.

Additional polyols that may be used in the esterification reaction described herein are glycerine, sorbitol, xylitol, erythritol and pentaerythritol. These materials may be reacted with fatty acids to produce mono- or diglycerides, sorbitol
15 esters, xylitol esters, etc. The reaction is especially useful for polyols which are not soluble in the fatty acid and which are not good solvents themselves.

The polyols can be esterified with any fatty acid or interesterified with a fatty acid ester or fatty acid
20 triglyceride. The fatty acids can be saturated, unsaturated, or polyunsaturated. In particular, those having from 8 to 24 carbon atoms are preferred for use herein. For the preparation of emulsifiers, those having from about 10 carbons to about 22 carbons are preferred. These include decanoic acid, dodecanoic
25 acid, stearic acid, palmitic acid, oleic acid, behenic acid, and others. Triglycerides of these acids can also be used. Lower alkyl esters, in particular, methyl and ethyl esters of the fatty acids, can be used as fatty acid sources.

The polyol and fatty acid are mixed together with an alkaline
30 catalyst. The alkaline catalyst can be the hydroxide of any of the alkaline earth metals, for example sodium, potassium or lithium hydroxide. The order of addition is not critical to the process.

The mole ratio of the polyol to fatty acid can range from
35 about 0.1:1 to about 3:1.

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An amount of the alkaline catalyst effective to catalyze the reaction is used. Preferably, an amount in the range of from about 0.01 to about 0.2 mole per mole of fatty acid used, most preferably from about 0.04 to about 0.10 mole per mole of fatty acid.

The fatty acid, the polyol and the catalyst are added to a reaction vessel which is held under an inert atmosphere. The inert atmosphere can be maintained by sparging the mixture, or by simply passing a non-reactive gas through the vessel. Inert (non-reactive) gases include nitrogen, helium, argon, etc. Under some conditions, water or carbon dioxide can act as the inert gas.

In order to produce a final product which has a good color and less off-odor, effective agitation is necessary. The agitation can be accomplished by any conventional means. This includes the use of a mechanical mixer as well as by inert gas sparging.

The esterification mixture is then heated to a temperature of from about 220°C to about 260°C, preferably from 225°C to 235°C. The vessel is held under atmospheric pressure or at a slight vacuum (508 mm to 760 mm of mercury absolute) or at a slight positive pressure (760 to 900 mm of mercury absolute). During the esterification reaction, the water is distilled off. The water is not returned to the reaction vessel. The reaction is monitored by measuring the free fatty acid level in the reaction mixture.

The free fatty acid level can be determined by titrating the free acid in aliquot portions.

When the free fatty acid level has been reduced to less than 1%, and preferably less than 0.5%, the pressure in the mixing vessel is reduced to less than about 127 mm of mercury, preferably less than 12 mm of mercury. The temperature is maintained at about 204°C to about 238°C. This reduction in pressure further strips the water from the mixture. The removal of the water also deodorizes the polyol ester.

The reaction mixture is held at full vacuum until substantially all of the water has been removed. The amount of time necessary to do this will, of course, depend on the size of

the reaction vessel and the vacuum system (e.g. pump or ejector systems). It can vary from 10 minutes to 4 hours. For example, a 68 kg. reaction mixture would be held at less than 127 mm of mercury for about 15 minutes. It is extremely important to
5 eliminate the water or minimize the water content to control the
interesterification and thus reversion to the more lipophilic esters.

The catalyst neutralization and the subsequent cooling steps also represent an improvement over the prior art.

10 After removal of the water, the catalyst is neutralized with a mild acid. For example, phosphoric acid, sodium di-hydrogen phosphate, acetic acid, citric acid, and other carboxylic acids can be used. Water can be present in the acid as water is readily removed because of the high temperatures and the vacuum.

15 The acid is added slowly to the reaction vessel. For example, a rate of from about 100 g/minute is suitable for a 45 kg. reaction batch. The pressure of less than 127 mm of Hg and the elevated temperatures (204°C to 238°C) are maintained during the neutralization to remove any water present. For maximum
20 efficiency, the acid is added through the bottom of the reaction vessel. The rate of acid addition is also affected by the water content in the acid and the effectiveness of the vacuum system.

Following the acid addition, the reaction mixture is cooled rapidly to less than 177°C. Preferably, the mixture is cooled to
25 less than 160°C. The rate of cooling should be at least 3°C to 15°C per minute, preferably 5°C to 12°C/minute. Once the temperature has reached about 145°C, the rate of cooling is no longer critical to the stability of the product.

Rapid cooling can be accomplished using a heat exchanger,
30 cooling coils or a water sparge. After the reaction mixture is cooled, any excess water is removed to minimize product deterioration during storage.

The minimizing of the water content before and during neutralization is critical to the formation of polyol esters which
35 have good color, odor, and flavor characteristics and which are

consistent in composition on a batch to batch basis. The rapid cooling of the reaction mixture minimizes the interesterification of the polyol esters.

Reversion, i.e. random rearrangement shifts in the composition, during and after processing can be detected by measuring the refractive index of the products or by analyzing the differential scanning calorimetry curve.

If a compositional shift has occurred in the product due to improper process control, the final refractive index reading will be significantly lower than the refractive index prior to neutralization and the peak height ratio of the differential scanning calorimeter curve will change. (Peak height ratio is defined below.)

Table 1 illustrates the changes that can occur in the peak height ratio measurements and in the refractive index. The seven samples, A through E, are all palmitic and stearic acid esters of hexapolyglycerol. They were prepared using about the same ratios of fatty acid, polyglycerol, sodium hydroxide, and phosphoric acid as in Example I. The scale of the reaction varied.

Samples C, D, E and G were prepared according to the process of this invention. Samples A and B were prepared using a process which was similar to that of Example I except that the pressure was not reduced prior to neutralization. The rearrangement that occurred in Samples A and B was a result of the high moisture conditions during this step of the process.

Sample F was prepared in the same manner as Sample G except that the reaction was cooled at the rate of about 1°C per minute. Because of this slow cooling, rearrangement occurred.

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TABLE 1

		% FREE FATTY ACID	REFRACTIVE INDEX*		PEAK HEIGHT RATIO**	
			Sample 1	Sample 2	Sample 1	Sample 2
5	A	less than 0.3	58.9	53.3	0.55	0.41
	B	less than 0.5	55.4	49.9	0.62	0.36
	C	less than 0.2	59.1	58.9	0.79	0.78
	D	less than 0.1	59.0	58.7	0.68	0.71
	E	less than 0.1	59.9	59.8	1.28	1.25
10	F	less than 0.2	60.2	52.0	-	-
	G	less than 0.5	60.9	60.0	-	-

*the butyro scale was used to measure the refractive index. Sample 1 is the sample before neutralization, Sample 2 is the final sample.

15 **Ratio of peak heights from the differential scaling calorimeter. Sample 1 is taken before neutralization, Sample 2 is taken after final cooling.

A. Refractive Index Measurement

Any refractometer can be used.

20 A Zeiss refractometer was used to measure the refractive index of the process samples. The refractometer is preheated and maintained at $60^{\circ} \pm 0.1^{\circ}\text{C}$ using a constant temperature water bath. Two samples are obtained from the reactor:

1. A sample prior to neutralization.
- 25 2. A sample after the reaction has cooled rapidly to 60°C to 82°C .

Sample 1 which is taken from the reactor before neutralization is rapidly cooled to 60°C and then the refractive index measured. Sample 2 is measured at 60°C . The standard refractive index method for the instrument is used.

30 B. Differential Scanning Calorimetry

Any differential scanning calorimeter can be used.

A duPont Model 990 thermal analyzer connected to a Model 910 differential scanning calorimeter was used to measure the peak height ratios of the process samples.

35 10.0 ± 0.1 mg of solid ester is placed in the sample cup. Most samples are more easily handled in their solid form. The

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lid is placed on the sample cup making sure that no material is on the sealing lip. The sample cup and lid are hermetically crimped using the sample crimper. A reference cell is prepared by crimping two lids on one empty sample cup.

- 5 The instrument controls are set as follows:

<u>Control</u>	<u>Setting</u>
X-Axis Zero Shift	0
X-Axis Scale	5°C/in.
Y-Axis Zero Shift	as required
10 Y-Axis Scale (Sensitivity)	2
Base line slope	0
Program mode	isothermal
Temperature rate	5°C/min.
Starting temp.	100°C

- 15 Allow the instrument to heat to 110°C to remove all the moisture in the cell. Reset the starting temperature to 20°C and allow the instrument to cool to 20°C (changing to isothermal control cools). Remove the cell cover and the silver lid from the cell. Place the sample pan on the rear thermocouple and the
- 20 reference pan on the front thermocouple. The same reference is left in place for all the tests. Allow the cell to equilibrate for approximately 2 to 3 minutes. Using the Y-Axis Zero control, position the pen to the starting point on the chart paper and move the pen to the down position to begin recording. Switch the
- 25 control program mode to Heat. It should take about 10 minutes to reach 70°C. When the temperature reaches 70°C, move the pen to the up position to stop recording and reset the starting temperature to 100°C and change to the isothermal mode. When the temperature reaches 100°C, remove the sample from the cell.
- 30 Repeat these same steps for the next sample.

Determination of the Peak Height Ratio

- The determination of the ratio of the two peaks produced by the instrument is done by first determining a base line. The base line is determined by extrapolating the line back from the
- 35 horizontal section of the curve tracing around the 60°C to 70°C

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mark. This extrapolated line, going back to the 30°C mark should be as straight and horizontal as possible. The height (number of blocks from base line to the top of the peak) of the first peak is divided by the height of the second peak to arrive at the ratio.

5 Determination of the peak temperatures

The determination of the differential scanning calorimeter peak temperatures is done by reviewing the heating mode differential scanning calorimeter scale cell of the polyol ester. The maximum point of each peak apex is extrapolated vertically to
10 the temperature axis (X-Axis). These temperature points are the peak temperature for each curve, respectively.

EXAMPLE I

Synthesis of a mixed ester of hexapolyglycerol.

A reaction vessel, sufficient to hold 50 kg. of reactant, is
15 used. The reaction vessel is fitted with a nitrogen sparge and a propeller mixer, is adapted to run under vacuum, and is also equipped with a condenser to collect the water removed during the reaction. To this vessel is added 27.67 kg. of polyglycerol having an average chain length of 6. The polyglycerol is mixed
20 with 0.43 kg. of 50% sodium hydroxide. The reaction mixture is then heated to about 115°C under full vacuum for about 15 minutes to remove the water from the sodium hydroxide polyglycerol mixture. Palmitic acid at a weight of 11.4 kg. (45.2 moles) and 6.12 kg. of stearic acid (21.5 moles) are added to the reaction
25 mixture at atmospheric pressure. A partial vacuum is then pulled on the reaction vessel (about 508 mm of mercury) and the vessel heated to about 220°C over the period of about an hour. The percent free fatty acid after an hour is about 6.3%. The vessel is then maintained at this partial pressure and at a temperature
30 of about 230°C for an additional 20 minutes when the free fatty acid drops to less than 0.3%.

The pressure is then lowered to about 12 mm of mercury and held there about for 15 minutes. This removes substantially all of the water from the reaction mixture. The temperature is then
35 maintained at about 224°C, the pressure maintained at 12 mm, and

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acid is added from the bottom. Over the period of about 5 minutes, 0.68 kg. of 75% phosphoric acid is added. The mixture is then cooled by using a water sparge and a 4.5°C cooling coil to a temperature of about 157°C over a period of about 7 minutes.

- 5 During this cooling, the water distills out of the reaction mixture. The water sparge is then stopped, and the mixture cooled by the cooling coil to about 93°C. The product is an opaque liquid which solidifies on further cooling.

- The total yield of the ester of the hexapolyglycerol is
10 40.6 kg. The weight of the distillate, including water collected during the reaction is 1.8 kg., approximately 0.9 kg. of this is water. The remainder is low molecular weight polyol. The saponification value is 98.74, and the hydroxyl value is 441.

- When this reaction is repeated using 27.66 kg. of the
15 polyglycerol having an average chain length of 6, 11.6 kg. palmitic acid, 6 kg. of stearic acid, essentially the same results are obtained. This product has a saponification value of 99.98 and a hydroxyl value of 430.

EXAMPLE II

- 20 A reaction vessel sufficient to hold 680 kg of reactant is used. The reaction vessel is fitted with nitrogen sparge, a propeller mixer, is adapted to run under vacuum, and is equipped with a condenser to collect the water removed during the reaction. To this vessel is added 394.6 kg of polyglycerol
25 having an average chain length of 6. The polyglycerol is mixed with 6.3 kg of sodium hydroxide catalyst (50% aqueous solution). The reaction mixture is then heated to 110°-116°C under full vacuum for approximately 10 to 15 minutes.

- The vacuum is released and 285.8 kg of stearic and palmitic
30 acid is added. The ratio of palmitic to stearic acid is 65:35. Nitrogen sparging is then started. The reaction is heated to about 229°C.

- Samples are removed from the reaction vessel periodically and titrated for free fatty acid. When the free fatty acid level is
35 below 1%, the pressure is lowered to a full vacuum (about 12 mm.

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of mercury) and held there for one hour. The vacuum is pulled slowly (to avoid foaming and excessive temperature drop). Substantially all the water is removed from the reaction mixture. Twenty pounds of phosphoric acid is then slowly added to the
5 reaction vessel at the rate of about one pound/minute.

Two to three minutes after the addition of the phosphoric acid, the vacuum is released and the system pressure reaches atmospheric. Nitrogen sparging is continuous. Water is injected into the vessel at the rate of 6.35 kg/minute over a 10 minute
10 period. This allows the reactor temperature to rapidly drop from 235°C to about 149°C. The cooling rate is about 8.5°C/minute. Once the product reaches 300°F, a vacuum (12 mmHg) is then pulled on the system and the system continues to cool at a reduced rate to 82.2°C.

15 The product has the following characteristics:

Refractive index	60.5 (butyro scale at 60°C)
Saponification value	101
Hydroxyl value	418
pH	7
20 Free fatty acid content	2%

1. B

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for esterifying a polyol comprising the steps of:
 - (1) reacting fatty acid and polyol under an inert atmosphere at temperatures of from about 220°C to about 260°C and an absolute pressure of from about 500 mm to about 900 mm of mercury, in the presence of an effective amount of alkaline catalyst;
 - (2) reducing the pressure to less than 127 mm of mercury when the free fatty acid level is less than 1% to remove substantially all the water;
 - (3) neutralizing the alkaline catalyst by slow addition of weak acid under reduced pressure and at a temperature of about 204°C to about 238°C; and
 - (4) rapidly cooling the reaction mixture to less than 177°C, at the rate of at least 3°C per minute, at reduced pressure of less than 127 mm of mercury.
2. A process according to Claim 1 wherein the mole ratio of polyol to fatty acid is from about 0.1:1 to about 3:1.
3. A process according to Claim 2 wherein the reaction step (1) is at a temperature of from 225°C to 235°C and a pressure of from about 500 mm to 760 mm and step 2 is at a pressure less than 13 mm of mercury.
4. A process according to Claim 3 wherein the alkaline catalyst is selected from the group consisting of potassium hydroxide, sodium hydroxide and lithium hydroxide.
5. A process according to Claim 4 wherein the mixture is cooled at the rate of at about 5°C to about 12°C per minute.
6. A process according to Claim 5 wherein the mixture is rapidly cooled in step (4) to a temperature of less than 160°C under reduced pressure.

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7. A process according to Claim 4 wherein the amount of alkaline catalyst is from about 0.01 to about 0.2 moles per mole of fatty acid.
8. A process according to Claim 3 wherein the polyol is a polyglycerol.
9. A process according to Claim 8 wherein the polyglycerol has from about 2 to about 15 glycerol moieties.
10. A process according to Claim 9 wherein the alkaline catalyst is selected from the group consisting of potassium hydroxide, sodium hydroxide and lithium hydroxide.
11. A process according to Claim 9 wherein the pressure is reduced in step (2) when the fatty acid level is less than 0.5%.
12. A process according to Claim 9 wherein the amount of alkaline catalyst is from about 0.01 to about 0.2 moles per mole of fatty acid.
13. A process according to Claim 12 wherein the alkaline catalyst is neutralized with phosphoric acid, acetic acid, or citric acid.
14. A process according to Claim 13 wherein the mixture is rapidly cooled in step (4) to a temperature of less than 160°C.
15. A process according to Claim 14 wherein the mixture is cooled at the rate of at least 3°C per minute.
16. A process according to Claim 3 wherein the polyol is selected from the group consisting of glycerol and sorbitol.
17. A process according to Claim 7 wherein the polyol is selected from the group consisting of glycerol and sorbitol.

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18. A process according to Claim 3 wherein the resulting esters are glyceride esters, sorbitol esters and sorbitan esters.

19. A process according to Claim 7 wherein the resulting esters are glyceride esters, sorbitol esters and sorbitan esters.



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